Indian J. Phys. **78A** (3), 377-379 (2004)

Note

Detection of crystal structure of chemically-deposited copper selenide thin films

Al-Mamun[1], S H Firoz[2] and A B M O Islam[1]*

[1]Department of Physics, University of Dhaka, Dhaka-1000, Bangladesh
[2]Institute of Glass and Ceramic Research and Testing
Bangladesh Council for Scientific and Industrial Research (BCSIR), Dhaka-1205, Bangladesh

E-mail : oislambd@yahoo.com

Received 28 August 2003, accepted 6 November 2003

Abstract : A low cost Chemical Bath Deposition (CBD) system has been developed in our laboratory for the preparation of copper selenide thin film. Good quality thin films of smooth surface of copper selenide thin films of compositions $Cu_{2-x}Se$ (x = 0.1–0.5) and Cu_3Se_2 were deposited using sodium selenosulfate as a source of selenide ions. Crystal structure of copper selenide ($Cu_{1.8}Se$ and Cu_3Se_2) thin films has been identified by X-ray diffraction (XRD) method. When the film is annealed at 250°C in air, the phases of $Cu_{1.8}Se$ and Cu_3Se_2 become crystalline, with structures of cubic (berzelianite) and tetragonal, respectively, whereas the as-deposited film was found to be disorder. The crystallinity is very low in as deposited samples, which improves on annealing in air at 250°C. The grain size of the as-deposited samples was very small, which was increased about 30% owing to annealing in air at 250°C.

Keywords : Chemical bath deposition, copper selenide, X-ray diffraction

PACS Nos. : 61.10.Nz, 68.55.Jk, 81.15.Gh

The term structure include a variety of concepts, which describe on various scales, the arrangement of the building blocks of materials. On an atomic scale, one deals with the crystal structure, which is defined by the crystallographic data of the unit cell. These data contain the shape and dimension of the unit cell and the atomic position within its Bravias structure. They are obtained by diffraction experiments. On a coaster scale, one deals with the microscopic observations of the microstructure, which characterizes the sizes, shapes and mutual arrangements of individual crystal grains. It also includes the microstructure and surface morphology of the materials. Suitable techniques are surface replication and scanning electron microscopy [1–4].

Frequently, one has to determine whether a given deposit is a single crystal or polycrystalline either with a random distribution of orientation with respect to the coating plane. For a single crystal coating, it is important to know its orientation relationship with respect to the substrate [5]. X-ray diffraction is a suitable tool to determine the crystal structure of any unknown materials, whether the sample is a single crystal or polycrystals [6]. $Cu_{2-x}Se$ is a kind of photovoltaic semiconductor, which can be used as a good absorber. In our previous study, we have reported that $Cu_{2-x}Se$ thin film has been successfully grown onto glass slide using CBD technique [7]. The resistivity is observed in the range $(2–25)\times10^{-3}$ Ω-cm from as-deposited to annealed $Cu_{2-x}Se$ film. The transmittance and reflectance is obtained to be about 3-75% and 4–20% in the wavelength range 400–1100 nm from as-deposited to annealed samples. In the present Note, we report the detection and structural study of $Cu_{1.8}Se$ and Cu_3Se_2 thin films using X-ray diffraction method.

The chemicals, used for the preparation of thin films, were LR grade (Merck) cupric chloride di-hydrate ($CuCl_2$, $2H_2O$), selenium powder of 99.99% purity, sodium sulfite (Na_2SO_3), tri-ethanol amine (TEA) and ammonium hydroxide (NH_4OH). At first, selenium was used for the preparation of sodium selenosulfate. Secondly, $CuCl_2$ $2H_2O$ solution was mixed with $NaSeSO_3$ at constant stirring. Then TEA was added to this solution. NH_4OH was used to adjust the pH of the reaction bath. Microscope glass slides were used as substrates. The substrates were cleaned well with detergent and distilled water, and were kept in H_2SO_4 for about 1h. They were then rinsed with distilled water and were dried in air prior to film deposition. The substrates were then immersed vertically into the deposition bath against the wall of the beaker containing the reaction mixture. After deposition at room temperature, the glass slides were taken

*Corresponding Author

out from the bath and then rinsed with distilled water and were dried in blowing air.

A Philips X'Pert X-ray diffractometer (XRD) was used to obtain X-ray data of the samples at the Bangladesh Council for Scientific and Industrial Research (BCSIR), where the powder diffraction technique was used with a primary beam power of 40 kV and 30 mA for Cu radiation. A nickel filter was placed before the sample to reduce CuK_β radiation and finally CuK_α radiation was only used as the primary beam. Here, sample-1 represents the as-deposited $Cu_{1.8}Se$ film followed by annealing at 250°C for one hour in air and sample-2 represents the as-deposited Cu_3Se_2 film followed by annealing at same condition.

All the X-ray diffraction data of the samples were analyzed using computer to get d values and peak intensities. The spacing d was calculated using Bragg relation

$$2d \sin\theta = \lambda ,$$

where λ is the wavelength of the incident radiation and for Cu($K\alpha$), λ = 1.54178Å. The XRD pattern was then analyzed using the d-values of their main fundamental peaks. The d-values and their intensity ratios were compared to the data available in the analytical library of the computer software, which contains JCPDS International Centre for Diffraction Data [8]. The unknown compounds and elements were identified from the observed data.

The XRD pattern of as-deposited $Cu_{1.8}Se$ film is shown in Figure 1. Lots of noise observed in the XRD pattern may be due to the growth of disorder film. The result has been presented here after slight removal of noise. From this pattern, it shows that no well-defined peak was found and no well-defined plane was obtained in the case of as-deposited films, which suggests that the as-deposited films were disorder. A little tendency of growing peak is found at an angle 2θ = 27.30°, 45.35° and 62.78°. The intensity of the observed peaks is very low, which become stronger due to annealing at 250°C.

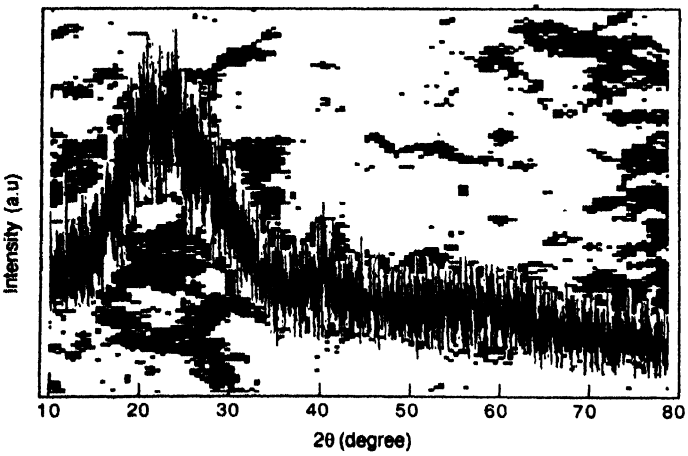

Figure 1. XRD pattern of as-deposited $Cu_{1.8}Se$ thin film.

The XRD pattern of sample-1 is shown in Figure 2. The XRD pattern shows well-defined peaks suggesting the formation of crystalline film due to annealing. A comparison of the observed pattern with the standard JCPDS (Joint Committee on Powder Diffraction Standards) cards shows that the annealed samples with above condition possess a structure, matching the cubic

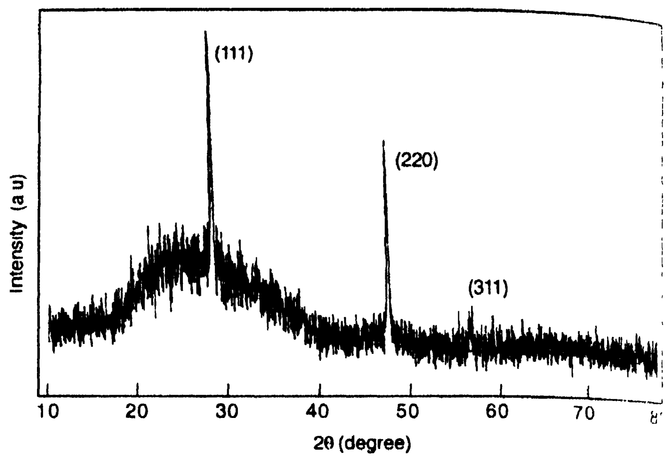

Fig. 2. XRD pattern of sample-1.

(berzelianite) (JCPDS 26-512) $Cu_{2-x}Se$ with x = 0.2, which belongs to the cubic system with lattice parameter a=5.697Å [9]. The crystallinity of the films was observed to improve owing to annealing at 250°C. The observed peak positions are in good agreement with those due to reflections from (111), (220) and (311) planes of the reported structure observed for as-deposited $Cu_{2-x}Se$ thin film prepared by $CuSO_4$ and tri-sodium citrate [10] and for as-deposited $Cu_{1.85}Se$ thin film of 0.13 μm thickness [11,12]. The XRD pattern of sample-2 is shown in Figure 3. It shows well-defined peaks matching to Cu_3Se_2 (JCPDS 25-263), which belongs to the tetragonal phase with a=5.63Å and c=11.23Å. The observed peak positions are also in good agreement with those due to reflections from (112), (204) and (312) planes of the reported structure [13]. It can be concluded that the crystallinity found is very low for as-deposited samples, which improves due to annealing in air at 250°C.

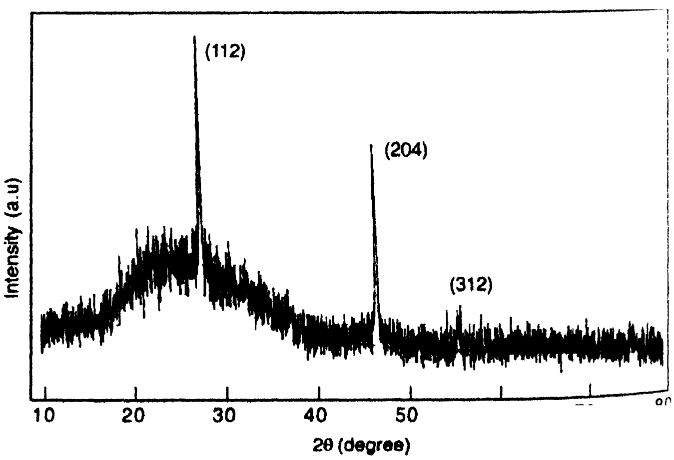

Fig. 3 XRD pattern of sample-2.

The crystalline grain size in the films was calculated using the Scherrer formula. The full width at half maxima (FWHM) of the largest peak for as-deposited sample was found to be 11.29 and that for the samples (1 and 2) were found to be 0.38 and 0.40, respectively. The average grain diameter for as-deposited sample was found to be 0.025 nm that increases to 0.724 and 0.688 nm in case of the samples 1 and 2, respectively. Very low grain size is observed for as-deposited samples, which was observed to increase about 30% owing to annealing. The X-ray diffraction parameters for samples-1 and 2 are summarized in Tables 1 and 2, respectively.

Table 1. X-ray diffraction parameters of sample-1

d (Å) Experimentally observed	*d* (Å) Theoretical values	*hkl*	Relative intensity (%)	Angle (2θ)	Peak height (counts/s)
3.324	3.328	111	100.00	27.43	125.12
1.996	2.038	220	88.08	45.14	110.20
1.743	1.738	311	29.99	53.36	37.52

Table 2. X-ray diffraction parameters of sample-2

d (Å) Experimentally observed	*d* (Å) Theoretical values	*hkl*	Relative intensity (%)	Angle (2θ)	Peak height (counts/s)
3.245	3.252	112	100.00	27.46	306.43
2.005	1.994	204	81.97	45.19	251.19
1.744	1.734	312	16.68	52.41	51.11

Our interest was to identify the newly formed compound on the glass slide and to determine its structure. Therefore, X-ray diffraction (XRD) is used for identification of $Cu_{2-x}Se$ and Cu_3Se_2 phases. When the film annealed at 250°C in air, the phases $Cu_{1.8}Se$ and Cu_3Se_2 become crystalline, with structures of cubic (berzelianite) and tetragonal, respectively, whereas the as-deposited film was found to be disorder. The observed peak positions are those due to reflections from (111), (220) and (311) planes for $Cu_{1.8}Se$ phase and (112), (204) and (312) planes for Cu_3Se_2 phase. The crystallinity is very low in as-deposited sample that improves on annealing in air at 250°C. The grain size of the as-deposited samples was very small, which was increased about 30% owing to annealing in air at 250°C.

Acknowledgments

The authors are grateful to the Director of Institute of Glass and Ceramic Research and Testing, BCSIR for allowing the XRD facilities. They acknowledge the financial support given from Bose Center for Advanced Study and Research in Natural Sciences, Dhaka University.

References

[1] C S Barrett and T B Massalski *Structure of Metals* (New York McGraw-Hill) (1966)

[2] L I Maissel and R Glang *Handbook of Thin Film Technology* (New York McGraw-Hill) (1970)

[3] P B Hirsch, A Howie, R B Nilcholson, D W Pashly and M J Whelan *Electron Microscopy of Thin Crystals* (Washington D C : Butterworths) (1965)

[4] L Stturkey *Symposium on Advances in Techniques in Electron Metallography* (American Society for Testing Materials) (1963)

[5] B K Vainshtein *Structure Analysis by Electron Diffraction* (New York· The Macmillan) (1970)

[6] B D Cullity *Elements of X-ray Diffraction* (New York· *Addison-Wesley*) (1959)

[7] Al–Mamun, A B M O Islam and A H Bhuiyan *Solar Energy Mater. Solar Cells* (in press)

[8] International Centre for Diffraction Data (PCPDFWIN, V **202** (1999)

[9] R Heyding and R M Murray *Can J Chem* **54** 841 (1976)

[10] M Lakshmi, K Bindu, S Bini, K P Vijaykumar, C Sudha Kartha, T Abe and Y Kashiwaba *Thin Solid Films* **386** 127 (2001)

[11] V M Garcia, P K Nair and M S T Nair *J Cryst Growth* **203** 113 (1999)

[12] E Andrade, V M García, P K Nair, M T S Nair, E P Zavala, L Huerta and M F Rocha *Instruments and Methods in Physics Research* B **161-163** 635 (2000)

[13] S H Johan, *Bull. Soc Fr. Mineral Crystallogr.* **94** 162 (1971)